



# AVAILABILITY OF MICRONUTRIENTS AND HEAVY METALS IN SOIL AS INFLUENCED BY INCORPORATION OF FLY ASH, ORGANIC MANURES AND INORGANIC FERTILIZERS UNDER MAIZE CULTIVATION

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## Abstract

An experiment was performed during *Kharif* season 2017-2018 in a Randomized Blocked Design with three replications for each treatment, taking organic manures, inorganic fertilizers and fly ash at their different doses, alone or in combination, to evaluate their impact on micronutrient heavy metals status in soil under maize (*Zea mays* L.) cultivation. FYM application in combination with inorganic fertilizers at their recommended doses (T2, 100% RDF + 100% FYM) exerted maximum positive influence on available Fe, Mn, Zn, Cu and Cr content in soil, followed by T5 (40% FA + 60% VC + 60% RDF). Within FA treatments, maximum concentrations of Fe, Mn, Zn, Cu and Cr were found at treatment T5 (40% FA) and their concentrations in soil decreased at low (T4, 20% FA) and higher (T6, T7 and T3: 60, 80 and 100 % FA, respectively) amount of FA incorporation into the soil. Ni, Co, Hg and Cd were found at non-detectable level in soil. The results also showed distinct differences between VC and FYM in their micronutrient content as well as their impact on DTPA extractable micronutrient in soil.

**Key words:** Fly ash, Organic manures, Fertilizers, Soil micro-nutrients, Heavy metals.

## Introduction

Fly-ash (FA), an amorphous ferro-alumino silicate, is known for its potential use in agriculture sector for the presence of plants macro- and micro-nutrients that boost crop yield (Arivazhagan *et al.*, 2011; Panda *et al.*, 2015), although its use in agricultural sector is limited as compared to other sectors (Kishor *et al.*, 2010). FA is reported to improve soil physicochemical properties (Sheoran *et al.*, 2014; Panda and Biswal, 2018) and hence soil fertility (Parab *et al.*, 2012; Kumar *et al.*, 2018; Kaur and Sukul, 2019). Its pH ranged from 4.5 to 12.0 depending on the sulphur and lime content of parental coal. FA is characterized with low amount of organic carbon, nitrogen and phosphorus but may often contain toxic heavy metals (Parab *et al.*, 2012; Verma *et al.*, 2016; Usmani *et al.*, 2017, Singh *et al.*, 2019). However, enhanced efficacy of FA may be achieved with its application with organic manures and fertilizers (Singh and Sukul, 2019), leading to increased bioconcentration of macro- and micro-

nutrients in plants (Rajashekhar *et al.*, 2017). Recently, there are several studies regarding its scope and utilization in agriculture sector. Several reports are available stating the impact of FA on their availability status of macronutrients in soil under cultivation of various crops (Pandey and Singh, 2010; Kumar and Jha, 2014; Panda and Biswal, 2018) and hence their beneficial influence over biomass production and increase in plant growth (Rajashekhar *et al.*, 2017; Kumar *et al.*, 2018). However, reports on influence of FA on micronutrient availability in soil is scanty. Keeping this under consideration, an attempt was made to evaluate the impact of FA alone or in combination with organic manures and fertilizers on the micronutrient and heavy metal status of the soil under maize cultivation.

## Materials and Methods

### Treatments

An experiment was performed in the research field of School of Agriculture, Lovely Professional University

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**Table 1:** DTPA-extractable micronutrients and heavy metals\* content in VC, FYM, FA and initial soil.

Properties	VC	FYM	FA	Soil
Iron (mg/kg)	836.5	1025.0	682.4	4.90
Manganese (mg/kg)	276.5	184.2	165.4	6.22
Zinc (mg/kg)	252.4	142.6	46.5	0.62
Copper (mg/kg)	46.0	32.5	26.50	1.52
Chromium (mg/kg)	14.5	11.2	9.8	0.62
* Ni, Hg, Co & Cd were found at non-detectable				

**Table 2:** Effect of FA, VC, FYM and RDF on DTPA extractable Fe, Mn, Zn and Cu content in soil.

Treatment	30 DAS	60 DAS	90 DAS	At harvest
<b>Fe (mg/kg)</b> [Initial value before application of any treatments: 4.90 mg/kg]				
T0	5.02 <sup>f</sup> ± 0.04	4.65 <sup>e</sup> ± 0.08	4.31 <sup>d</sup> ± 0.06	4.16 <sup>c</sup> ± 0.08
T1	5.33 <sup>bc</sup> ± 0.05	4.94 <sup>abcd</sup> ± 0.09	4.59 <sup>abc</sup> ± 0.06	4.40 <sup>abc</sup> ± 0.09
T2	5.55 <sup>a</sup> ± 0.05	5.14 <sup>a</sup> ± 0.09	4.79 <sup>a</sup> ± 0.07	4.58 <sup>a</sup> ± 0.06
T3	5.08 <sup>ef</sup> ± 0.04	4.71 <sup>de</sup> ± 0.09	4.37 <sup>d</sup> ± 0.05	4.20 <sup>c</sup> ± 0.07
T4	5.43 <sup>b</sup> ± 0.05	4.99 <sup>abc</sup> ± 0.07	4.64 <sup>ab</sup> ± 0.08	4.45 <sup>abc</sup> ± 0.05
T5	5.51 <sup>a</sup> ± 0.05	5.07 <sup>ab</sup> ± 0.09	4.71 <sup>a</sup> ± 0.07	4.52 <sup>ab</sup> ± 0.09
T6	5.25 <sup>cd</sup> ± 0.03	4.84 <sup>bcd</sup> ± 0.06	4.49 <sup>bcd</sup> ± 0.09	4.31 <sup>abc</sup> ± 0.08
T7	5.17 <sup>de</sup> ± 0.02	4.76 <sup>cde</sup> ± 0.05	4.43 <sup>cd</sup> ± 0.04	4.25 <sup>bc</sup> ± 0.03
<b>Mn (mg/kg)</b> [Initial value before application of any treatments: 6.22 mg/kg]				
T0	6.32 <sup>e</sup> ± 0.05	5.86 <sup>d</sup> ± 0.10	5.43 <sup>e</sup> ± 0.06	5.22 <sup>c</sup> ± 0.10
T1	6.71 <sup>bc</sup> ± 0.06	6.21 <sup>abcd</sup> ± 0.11	5.77 <sup>bcd</sup> ± 0.05	5.54 <sup>abc</sup> ± 0.11
T2	6.99 <sup>a</sup> ± 0.07	6.48 <sup>a</sup> ± 0.11	6.05 <sup>a</sup> ± 0.09	5.80 <sup>a</sup> ± 0.11
T3	6.45 <sup>de</sup> ± 0.03	5.99 <sup>cd</sup> ± 0.10	5.56 <sup>de</sup> ± 0.08	5.34 <sup>bc</sup> ± 0.13
T4	6.85 <sup>ab</sup> ± 0.04	6.31 <sup>abc</sup> ± 0.11	5.87 <sup>abc</sup> ± 0.04	5.63 <sup>ab</sup> ± 0.10
T5	6.93 <sup>a</sup> ± 0.07	6.38 <sup>ab</sup> ± 0.12	5.93 <sup>ab</sup> ± 0.09	5.69 <sup>ab</sup> ± 0.11
T6	6.66 <sup>c</sup> ± 0.05	6.13 <sup>abcd</sup> ± 0.11	5.70 <sup>bcd</sup> ± 0.03	5.47 <sup>abc</sup> ± 0.11
T7	6.58 <sup>cd</sup> ± 0.06	6.06 <sup>bcd</sup> ± 0.10	5.63 <sup>cde</sup> ± 0.08	5.40 <sup>bc</sup> ± 0.10
<b>Zn (mg/kg)</b> [Initial value before application of any treatments: 0.62 mg/kg]				
T0	0.70 <sup>f</sup> ± 0.01	0.67 <sup>e</sup> ± 0.04	0.59 <sup>f</sup> ± 0.04	0.56 <sup>g</sup> ± 0.04
T1	0.92 <sup>e</sup> ± 0.01	0.88 <sup>c</sup> ± 0.02	0.79 <sup>e</sup> ± 0.01	0.76 <sup>d</sup> ± 0.02
T2	1.13 <sup>a</sup> ± 0.01	1.08 <sup>a</sup> ± 0.02	0.97 <sup>a</sup> ± 0.02	0.93 <sup>a</sup> ± 0.01
T3	0.76 <sup>e</sup> ± 0.02	0.71 <sup>e</sup> ± 0.03	0.65 <sup>e</sup> ± 0.01	0.62 <sup>f</sup> ± 0.06
T4	0.95 <sup>c</sup> ± 0.04	0.90 <sup>c</sup> ± 0.06	0.82 <sup>c</sup> ± 0.01	0.80 <sup>c</sup> ± 0.01
T5	1.05 <sup>b</sup> ± 0.04	0.99 <sup>b</sup> ± 0.02	0.90 <sup>b</sup> ± 0.03	0.86 <sup>b</sup> ± 0.01
T6	0.86 <sup>d</sup> ± 0.05	0.81 <sup>d</sup> ± 0.02	0.73 <sup>d</sup> ± 0.01	0.71 <sup>e</sup> ± 0.04
T7	0.78 <sup>e</sup> ± 0.01	0.72 <sup>e</sup> ± 0.03	0.68 <sup>e</sup> ± 0.02	0.63 <sup>f</sup> ± 0.01
<b>Cu (mg/kg)</b> [Initial value before application of any treatments: 1.52 mg/kg]				
T0	1.60 <sup>g</sup> ± 0.023	1.54 <sup>f</sup> ± 0.037	1.41 <sup>g</sup> ± 0.023	1.37 <sup>e</sup> ± 0.02
T1	1.83 <sup>cd</sup> ± 0.029	1.76 <sup>bcd</sup> ± 0.040	1.61 <sup>cd</sup> ± 0.029	1.56 <sup>bc</sup> ± 0.03
T2	2.02 <sup>a</sup> ± 0.029	1.94 <sup>a</sup> ± 0.043	1.79 <sup>a</sup> ± 0.032	1.71 <sup>a</sup> ± 0.04
T3	1.66 <sup>fg</sup> ± 0.023	1.60 <sup>ef</sup> ± 0.037	1.46 <sup>fg</sup> ± 0.024	1.42 <sup>de</sup> ± 0.03
T4	1.89 <sup>bc</sup> ± 0.029	1.81 <sup>bc</sup> ± 0.043	1.65 <sup>bc</sup> ± 0.029	1.62 <sup>ab</sup> ± 0.05
T5	1.96 <sup>ab</sup> ± 0.029	1.87 <sup>ab</sup> ± 0.044	1.72 <sup>ab</sup> ± 0.032	1.68 <sup>a</sup> ± 0.04
T6	1.78 <sup>de</sup> ± 0.026	1.70 <sup>cde</sup> ± 0.040	1.56 <sup>de</sup> ± 0.026	1.53 <sup>bc</sup> ± 0.03
T7	1.72 <sup>ef</sup> ± 0.023	1.64 <sup>def</sup> ± 0.040	1.51 <sup>ef</sup> ± 0.026	1.47 <sup>cd</sup> ± 0.02
Values are in Mean ± SD; (n = 3). Different letters in the same row represent significant differences of different treatments at p < 0.05 according to Duncan's Multiple Range Test (One-way ANOVA followed by Tukey's test).				

during *Kharif* season 2017-2018, in a Randomized Blocked Design with three replications for each treatment. There were total eight treatments including control. Recommended dose of fertilizers (RDF) for N, P and K were used as 180, 60 and 40 kg/ha, respectively. Farmyard manure (FYM), vermicompost (VC) and FA were applied to the field @16, 5 and 20 t/ha. These treatments include control (T0, no RDF, no FYM, no VC, no FA), T1 (100% RDF + 100% VC), T2 (100% RDF + 100% FYM), T3 (100% FA), T4 (20% FA + 80% RDF + 80% VC), T5 (40% FA + 60% RDF + 60% VC), T6 (60% FA + 40% RDF + 40% VC), T7 (80% FA + 20% RDF + 20% VC).

### Cultural practices

Maize seeds (Kawari 50) were sown by dibbling method, keeping plant to plant and row to row distance as 20 cm and 60 cm, respectively. FA, VC, FYM and full dose of DAP and MOP were added during the final field preparation and urea was applied as basal and 2 splits.

### Soil sample preparation and estimation of trace elements

Soil samples were taken before application of any soil amendment and after soil treatments at different time intervals [30, 60, 90 DAS (days after sowing) and at harvest]. The soil samples were air dried, ground and screened through a 2 mm sieve. Micronutrients *viz.* Fe, Mn, Zn & Cu and heavy metals *viz.* Cr, Ni, Co, Hg and Cd in soil were extracted with 0.005(M) DTPA solution (pH 7.3) (Lindsay and Norvell, 1978) and were measured with the help of an Atomic Absorption Spectrophotometer [model: PerkinElmer PinAAcle 900F with FIAS100] from M/S PerkinElmer (India) Pvt. Ltd.]. Micronutrients and heavy metals content in VC, FYM, FA and initially in soil before application of any soil amendments are summarized in table 1.

### Statistical analysis

Duncan Multiple Range Test (DMRT) was applied to identify the most efficient treatment. Anova was done to test the significance of difference for

**Table 3:** Effect of FA, VC, FYM and RDF on DTPA-extractable heavy metal, Cr (mg/kg) in soil\*

Treatment	30 DAS	60 DAS	90 DAS	At harvest
T0	0.63 <sup>f</sup> ±0.014	0.58 <sup>g</sup> ±0.008	0.51 <sup>e</sup> ±0.008	0.46 <sup>f</sup> ±0.011
T1	0.89 <sup>c</sup> ±0.020	0.83 <sup>d</sup> ±0.015	0.77 <sup>b</sup> ±0.014	0.73 <sup>d</sup> ±0.020
T2	1.14 <sup>a</sup> ±0.026	1.05 <sup>a</sup> ±0.017	0.95 <sup>a</sup> ±0.03	0.92 <sup>a</sup> ±0.026
T3	0.71 <sup>e</sup> ±0.017	0.66 <sup>f</sup> ±0.012	0.61 <sup>d</sup> ±0.012	0.58 <sup>e</sup> ±0.014
T4	0.93 <sup>c</sup> ±0.023	0.88 <sup>c</sup> ±0.17	0.81 <sup>b</sup> ±0.014	0.79 <sup>c</sup> ±0.020
T5	1.04 <sup>b</sup> ±0.023	0.97 <sup>b</sup> ±0.017	0.91 <sup>a</sup> ±0.020	0.85 <sup>b</sup> ±0.023
T6	0.82 <sup>d</sup> ±0.017	0.76 <sup>e</sup> ±0.014	0.71 <sup>c</sup> ±0.014	0.67 <sup>d</sup> ±0.017
T7	0.73 <sup>e</sup> ±0.017	0.69 <sup>f</sup> ±0.012	0.63 <sup>d</sup> ±0.012	0.60 <sup>e</sup> ±0.014

\* Ni, Hg, Co & Cd were found non-detectable.  
Initial value of Cr in soil before application of any treatments: 0.62 mg/kg.  
Values are in Mean ± SD; (n = 3). Different letters in the same row represent significant differences of different treatments at p < 0.05 according to Duncan's Multiple Range Test (One-way ANOVA followed by Tukey's test).

each parameter. Calculation was done at 5% significant level.

### Results and Discussion

The results of micronutrients viz., Fe, Mn, Zn and Cu and heavy metals viz., Cr, Ni, Co, Hg and Cd from soil are summarized in table 2 and 3, respectively. Ni, Co, Hg and Cd were found at non-detectable level in VC, FYM, FA and in both initial and amended soil. This might be attributed to their dilution effect. Since initial soil analysis before addition of any soil amendments exhibited non-detectable levels of Ni, Co, Hg and Cd, it may be concluded that addition of organic and inorganic fertilizers and FA, either alone or in combination, showed no effect in the accumulation of such heavy metals in soil. In the present investigation, concentrations of all detectable micronutrients and heavy metal obtained at 30 DAS were above the initial values (Fe, 4.90 mg/kg; Mn, 6.22 mg/kg; Zn, 0.62 mg/kg; Cu, 1.52 mg/kg; Cr, 0.52 mg/kg) and a decreasing trend in their concentration was observed with progress of time. This may be explained by plant uptake or by gradual conversion of their soluble to insoluble form in soil. However, conversion of available to unavailable form by the influence of soil amendments may be ruled out, as same trend was found in control treatment also. In case of all elements, when different treatments were compared with each other, same trend was obtained at 30, 60, 90 DAS and after harvest where T2 showed highest concentration and T0 lowest. The trend was observed as: T2>T5>T4>T1>T6>T7>T3>T0. Within FA treatments, maximum concentrations of Fe, Mn, Zn, Cu and Cr were found at treatment T5 (40% FA) and their concentrations in soil decreased at low (T4, 20% FA) and higher (T6, T7 and T3: 60, 80 and 100% FA, respectively) amount of FA incorporation into the soil. It was also observed that VC and FYM differed within themselves in respect of their own micronutrient and heavy metal content (Table 1) and their effect on the DTPA extractable Fe, Mn, Zn, Cu and Cr content in soil

(Table 2 and 3), which is well in agreement with earlier report (Ravimycin, 2016). Addition of organic manures to soil showed significant influence on the availability of micronutrients in soil, which might be due to microbial activity and their diversity (Azarmi *et al.*, 2008; Ravimycin, 2016) and changes in soil pH (Jordao *et al.*, 2006). This agrees with our findings where soils initially at 30 DAS showed an increase in all tested micronutrients and heavy metal (Cr). FA was also reported to influence the availability of micronutrients in soil (Mishra *et al.*, 2007). They reported a progressive

increase in the levels of Mn, Zn and Cu with various FA levels in soil with difference in the rate of increase of individual elements. However, in their study, heavy metals Cr and Cd were found below the level of detection. But in our experiment, Ni, Co, Hg and Cd were found at non-detectable level, while Cr was detected in all treatments. Phung *et al.*, (1979) observed a decrease in the release of Fe, Mn, Ni, Co and Pb in acid soils with addition of highly alkaline FA. But mixing of alkaline FA in alkaline soils did not exhibit any effect on their release. Furthermore, alkaline FA in acid soils enhanced the mineralization of organic matter and thus, promotes nutrient supplying capacity by raising the pH level of the soil (Khan *et al.*, 1996). It was reported that application of FA with lime and FYM would be beneficial as they inhibited the heavy metal solubility in soil and heavy metal (Pb, Cd, Cr) concentrations in different FA treated soils were found below toxic level (Chandrakar *et al.*, 2018). Application of FYM also exhibited significant increase in the DTPA extractable micronutrients in various soil depths (Chaudhary and Narwal, 2005). However, the surface layer showed higher increase than that in the lower depths. In the present investigation, when results from soils at harvest were compared with initial micronutrient and heavy metal status, a tendency of Zn, Cu and Cr accumulation in case of majority of the treatments was envisaged, highlighting a need for long-term field trials.

### Conclusion

All treatments of soil amendments showed significant positive influence over control treatment in respect of increasing availability of Fe, Mn, Zn, Cu and Cr at the initial stage of the experiment (30 DAS) as compared to the initial soil before application of any treatment. However, later a decreasing trend in their concentration was observed with progress of time. Treatment containing 100% RDF and 100% FYM exhibited the maximum impact on the DTPA soluble micronutrient and heavy

metal. Within FA treatments, maximum concentrations of micronutrients and heavy metal were found at treatment T5 (40% FA) and interestingly, their concentrations in soil were alleviated at lower (T4, 20% FA) and higher (T6, T7 and T3: 60, 80 and 100 % FA, respectively) doses of FA incorporation into the soil. As organic manures do not pollute the environment, rather improve the physical properties of soils and help in acquiring sustainable agriculture; it is recommended to use organic manures along with inorganic fertilizers. The present investigation also revealed that application of organic manure along with inorganic fertilizers and FA increases the micronutrient status of the soil. However, reports are also available stating that the soil available Cu, Mn and Fe content were not significantly influenced by different combination of FYM, FA and Fertilizers. standardization of the amount of FA to be incorporated in soil is very much needed because incorporation of low or high amount of FA may exert negative impact as envisaged by the present investigation and this may lead to alteration in physicochemical properties affecting the overall crop growth and yield. Thus, due to well pronounced integrated effect of FA, manures and fertilizer to improve the soil nutrient status, for safe and ecofriendly disposal as well as for the improvement of the soil condition, FA should be considered, keeping a strict vigil on its amount of incorporation.

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